**CLAPEYRON'S EQUATION**

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**CLAPEYRON'S EQUATION**

Clapeyron's equation expresses the relationship between temperature (T) and pressure (P) to maintain univariant assemblages in equilibrium. Thus, this equation expresses the stability relation between reactant and product phases as a function P and T for a system at constant composition, which may be one of the most important keys to understanding the geochemical processes on the Earth. For example, the three polymorphs of Al2SiO5, andalusite, kyanite, and sillimanite, occur in the rocks that have experienced different metamorphic conditions, but are rarely present together. The stability relations among the polymorphs indicate that the rocks containing kyanite should have experienced relatively high-pressure and low-temperature metamorphism, while andalusite is indicative of relatively low-pressure and high-temperature conditions. Clapeyron's equation is useful for gaining a qualitative understanding of such stability relations among phases and in constructing phase diagrams with Schreinemakers rule (see Nordstrom and Munoz, 1985 and Philpotts, 1990).

Clapeyron's equation can be easily developed from the Gibbs free energy change of a reaction as a function of T and P. Consider a reaction at T1 and P1. At equilibtium,

Grxn(T1,P1) = 0, (1)

where Grxn(T1,P1) is the Gibbs free energy change of the reaction at T1 and P1. If now T and P vary by the amount dT and dP to reach T2 and P2, the Gibbs free energy change for the reaction varies by the amount d(Grxn) and the new equilibrium condition will be:

Grxn(T2,P2) = Grxn(T1,P1) + d(Grxn) = 0. (2)

From equations (1) and (2),

d(Grxn) = 0. (3)

d(Grxn) may be expressed in a differential form:

. (4)

Since  where Srxn and Vrxn are respectively the entropy change and the volume change of the reaction, equation (4) becomes

d(G)rxn = - SrxndT + VrxndP. (5)

From equations (3) and (5),

 . (6)

If the reaction reaches an equilibrium state, rxn = TSrxn where Hrxn is the enthalpy change of the reaction. Equation (6) can be rewritten as

. (7)

Equations (6) and (7) are alternative forms of the Clapeyron's equation, named after French scientist Benoit Pierre Emile Clapeyron (1799-1864) who was the first to appreciate the importance of Carnot's work on the conversion of heat into work (Clapeyron 1833).

Clapeyron's equation shows that if T of a system in equilibrium at constant composition varies by an amount dT, equilibrium can only be maintained if P varies by an amount dP such that

 (8)

In other words, Clapeyron's equation indicates the instantaneous slope of a univariant line (or phase stability boundary) of the phase diagram at given T and P. It should be noted that Clapeyron's equation is meaningful only if S and V are not simultaneously zero. For example, second order polymorphic transformations like order-disorder transformation of fayalite, which are characterized by discontinuities in the second derivatives of free energy, exhibit S=0 and V=0 and can not be studied in terms of Clapeyron's equation.

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**Cross-References:** *Enthalpy; Entropy; Equilibrium; Free Energy; Metamorphism; Phase Equilibria.*